Polarization Dependence of Optical Transitions in Graphene Nanoribbons

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The universality of k-dependent electron-photon and electron-phonon matrix elements is discussed for graphene nanoribbons and carbon nanotubes. An electron undergoes a change in wavevector in the direction of broken translational symmetry, depending on the light polarization direction. We suggest that this phenomenon originates from a microscopic feature of chirality.

Recently, graphene nanoribbons (GNRs) have attracted attention for a variety of reasons.[1–3] GNRs are considered as unrolled carbon nanotubes (CNTs), and a characteristic of GNRs (CNTs) is induced by the existence (absence) of edges.[4–6] GNRs as well as CNTs are categorized by chirality,[7] and armchair GNRs (A-GNRs) and zigzag GNRs (Z-GNRs) are known to have a high symmetry [see Fig. 1(a) and (b)]. Several experimental groups have attempted to clarify the optical properties of GNRs.[8,9] Knowing the optical selection rule for GNRs will be an important step in understanding GNRs. Theories suggest that A- and Z-GNRs exhibit different polarization dependence as regards optical absorption.[10–12] Namely, the selection rule for Z-GNRs possesses a 90° rotation of polarization with respect to the selection rule for A-GNRs. This polarization dependence originates from the chirality dependent electronic wavefunction for GNRs.[4–6] However, the derivations of the chirality dependence described so far are complicated, inaccessible, and do not make it easy to grasp the essential point of the problem. The purpose of this paper is to explain the selection rules for A-GNRs, Z-GNRs, and CNTs in a unified manner. The procedure adopted in this paper is not only simple but also applicable to obtaining selection rules even for electron-phonon interactions.

First, we explain that the optical selection rule for A-GNRs is the same as that for CNTs. The electron-photon interaction is given by $\mathbf{A}(\mathbf{r}, t) \cdot \hat{\mathbf{J}}$, where $\mathbf{A}(\mathbf{r}, t)$ and $\hat{\mathbf{J}}$ are a vector potential and a current operator, respectively. In the dipole approximation, we assume a current operator of the form $\hat{\mathbf{J}} = -(e/m)\hat{\mathbf{p}}$, where $-e$ is the electron charge, m is the electron mass, and $\hat{\mathbf{p}} = -i\hbar\nabla$ is the momentum operator. This current operator does not take the degree of sublattice (chirality) into account. Later we provide a proper matrix element for the current operator that takes account of the chirality of graphene. The importance of chirality will be clearly understood with this line of argument.

Let us review CNTs. As a result of the cylindrical geometry of CNTs, the wavevector (k) around the axis of a tube is a good quantum number, and the wavefunction
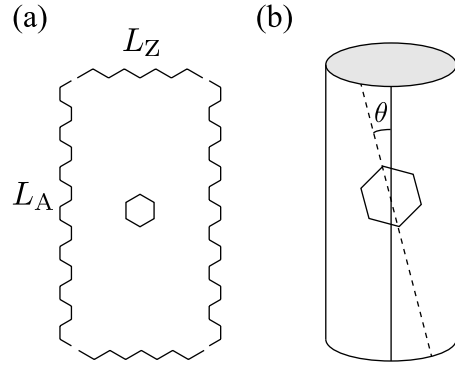

Fig. 1. (a) Chirality of a GNR. A large aspect ratio $L_A/L_Z \gg 1$ ($L_Z/L_A \gg 1$) defines an armchair (zigzag) GNR, where L_A and L_Z denote the lengths of the armchair and zigzag edge, respectively. (b) The chirality of a CNT is defined by the angle θ with respect to the direction of the CNT axis.

of an electron can be taken as a plane wave if we omit the sublattice of graphene,

$$\psi_k(x) = \frac{1}{\sqrt{L}}e^{ikx}, \qquad (1)$$

where x and L are the circumferential coordinate and length, respectively. The wavevector is quantized by the periodic boundary condition $\psi_k(x + L) = \psi_k(x)$ as $k_n L = 2\pi n$ (n are integers), so that the electronic modes are labeled by the band index n as $\psi_n(x)$. The optical selection rule for the nth and mth states is related to the possible change in wavenumber, $\Delta n \equiv m - n$. The cylindrical geometry of CNTs gives rise to a positional x-dependence for the vector potential A_x,[13] that is, for a light whose polarization direction is perpendicular to the CNT axis,

$$A_x(x) = A \sin\left(\frac{2\pi}{L}x\right). \qquad (2)$$

Then we see that Δn must be ± 1 in order to have a nonzero matrix element of $-(e/m)\oint A_x(x)\psi_m^*(x)\hat{p}_x\psi_n(x)dx$. This condition for wavenumber $\Delta n = \pm 1$ is the selection rule of CNTs with a perpendicularly polarized light.[13–15]

With GNRs, a plane wave is reflected at the edge. Consequently a standing wave is formed by the superposition of two plane waves propagating in opposite directions. Suppose that an incident wave has the wavevector k in the direction perpendicular to the edge, then the wavevector of the reflected wave is given by $-k$ as a result of momentum conservation. There are two possible types of superpositions: $\psi_k(x) \pm \psi_{-k}(x)$. For A-GNRs, the electron wavefunction should vanish at the edge ($x = 0$), and only the antisymmetric combination,

$$\varphi_k(x) = \sqrt{\frac{2}{L}} \sin(kx), \qquad (3)$$

is selected. The boundary condition should be also imposed at $x = L$ as $\varphi_k(L) = 0$, which gives $k_n = \pi n/L$ (n are positive integers). The standing waves are labeled by the band index n as $\varphi_n(x)$. The flat geometry of GNRs results in a constant vector potential $A_x(x) = A$, and the matrix elements are given by $-(e/m)A \int_0^L \varphi_m(x)\hat{p}_x\varphi_n(x)dx$. This integral results in

$$\frac{2}{L}\int_0^L \sin(k_m x)\cos(k_n x)dx$$

$$= \begin{cases} 0 & m - n \in \text{even} \\ \dfrac{2}{\pi}\left(\dfrac{1}{m-n} + \dfrac{1}{m+n}\right) & m - n \in \text{odd.} \end{cases} \qquad (4)$$

Because the Fermi wavevector satisfies $k_F = 4\pi/3a$ (a denotes a lattice constant), the values of m and n are selected so that they are large enough for $(m+n)^{-1}$ to be negligible compared with $(m-n)^{-1}$. Thus, we approximate $\frac{2}{L}\int_0^L \sin(k_m x)\cos(k_n x)dx = (2/\pi)\Delta n^{-1}$. Furthermore, the transition amplitudes for $\Delta n = \pm 3, \pm 5, \ldots$ are suppressed by the factor of Δn^{-1}. The selection rule of A-GNRs is mainly given by $\Delta n = \pm 1$, which is coincident with the selection rule of CNTs as discussed above.

It is meaningful to consider the reason for the similarity. For CNTs, the change in electron wavenumber ($\Delta n = \pm 1$) is brought about by the macroscopic topology of the cylinder. A light behaves as a standing wave on a cylindrical surface [eq. (2)], while the electrons are plane waves [eq. (1)]. For GNRs, the electrons are standing waves [eq. (3)], while the light is a uniform plane wave (i.e., zero-wavenumber mode). An essential factor in obtaining $\Delta n = \pm 1$ for A-GNRs is that the momentum operator $\hat{p}_x$ alters $\sin(kx)$ into $\cos(kx)$. Since the momentum operator originates from a lattice spacing as $\varphi_n(x + a/2) - \varphi_n(x - a/2) \approx a(\partial/\partial x)\varphi_n(x)$, we see that a microscopic lattice topology is essential for a change in the electron wavenumber. Contrastingly, a plane wave satisfies $a(\partial/\partial x)\psi_n(x) \propto \psi_n(x)$, and the orthogonality condition tells us that the corresponding current cannot change the electron wavenumber when $A_x(x)$ is constant. Therefore, as long as standing waves are formed in GNRs, we expect the wavnumber to change in an optical transition. A change in the wavenumber will be a universal phenomenon for GNRs, as we see in the following.

To investigate the polarization dependence of the selection rule, we now take account of the local arrangement of the carbon-carbon bonds on an atomic scale [see
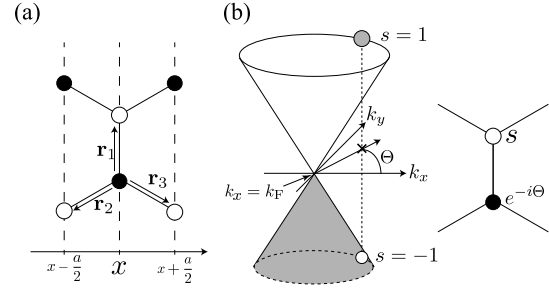

Fig. 2. (a) The bond vectors, $\mathbf{r}_1 = a_{cc}\mathbf{e}_y$, $\mathbf{r}_2 = a_{cc}(-\frac{\sqrt{3}}{2}\mathbf{e}_x - \frac{1}{2}\mathbf{e}_y)$, and $\mathbf{r}_3 = a_{cc}(\frac{\sqrt{3}}{2}\mathbf{e}_x - \frac{1}{2}\mathbf{e}_y)$, where a_{cc} denotes the bond length. (b) The band index s in the Dirac cone, and the relative amplitude between two sublattices is determined by s and Θ, respectively. These variables correspond to the amplitudes at two sublattices.

Fig. 2(a)]. Since graphene's hexagonal unit cell consists of two atoms (A and B), the wavefunction has two components

$$\Psi_{k_n k_y s}(\mathbf{r}_A) = \begin{pmatrix} \Psi^A_{k_n k_y s}(\mathbf{r}_A) \\ \Psi^B_{k_n k_y s}(\mathbf{r}_A + \mathbf{r}_1) \end{pmatrix}$$

$$= \varphi_n(x)\psi_{k_y}(y)\frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\Theta(k_n, k_y)} \\ s \end{pmatrix}, \qquad (5)$$

where s is the band index ($+1$ for the conduction band, -1 for the valence band), $\mathbf{r}_A = (x, y)$ denotes the position of an A-atom, $\mathbf{r}_a$ ($a = 1, 2, 3$) represents the bond vectors [see Fig. 2(a)], and Θ is the polar angle in (k_x, k_y) plane defined with respect to the Dirac point at $(k_F, 0)$, as shown in Fig. 2(b). The current also consists of two components: $\mathbf{J}^A(\mathbf{r}_A)$ and $\mathbf{J}^B(\mathbf{r}_B)$, where $\mathbf{J}^A(\mathbf{r}_A)$ [$\mathbf{J}^B(\mathbf{r}_B)$] represents the electron's flow into an A-atom [B-atom] at $\mathbf{r}_A$ [$\mathbf{r}_B$] from the nearest-neighbor B-atoms [A-atoms]. These components contribute to a local dipole moment and are essential to the optical transition.[16] An optical transition in each sub-atom does not induce a local dipole moment and can be omitted from the analysis.

Suppose that an incident light transfers an electron from the B-sites denoted by open circles in Fig. 2(a), to the central A-site (solid circle). The corresponding current component is given by

$$\mathbf{J}^A_{k_m k'_y s', k_n k_y s}(\mathbf{r}_A) = ie\frac{\gamma}{\hbar}\Psi^A_{k_m k'_y s'}(\mathbf{r}_A)^\dagger \times$$

$$\left\{\sum_{a=1,2,3} \mathbf{r}_a \Psi^B_{k_n k_y s}(\mathbf{r}_A + \mathbf{r}_a)\right\}, \qquad (6)$$

where γ denotes the nearest-neighbor hopping integral. By putting eq. (5) into eq. (6), we obtain $\int \mathbf{J}^A_{k_m k'_y s', k_n k_y s}(\mathbf{r})dy = \delta_{k'_y k_y}\frac{s}{2}e^{i\Theta(k_m, k_y)}\mathbf{j}^A_{mn}(x)$, where

$$\mathbf{j}^A_{mn}(x) = ie\frac{\gamma}{\hbar}\varphi_m(x) \times \left\{\mathbf{r}_1\varphi_n(x) + \mathbf{r}_2 e^{-ik_y(3a_{cc}/2)}\varphi_n(x - \frac{a}{2})\right.$$

$$\left. + \mathbf{r}_3 e^{-ik_y(3a_{cc}/2)}\varphi_n(x + \frac{a}{2})\right\}. \qquad (7)$$

Because $e^{-ik_y(3a_{cc}/2)}$ is approximately equal to 1 for the states near the Dirac point, we set $e^{-ik_y(3a_{cc}/2)} = 1$ in eq. (7).[12] Thus, k_y does not appear explicitly in the

following analysis for A-GNR, but it is implicitly taken into account through $\Theta(k_n, k_y)$. Here let us define the amplitude for an A-atom of GNR $[\alpha_i]_{mn} = \int A_i(x)\mathbf{e}_i \cdot \mathbf{j}^A_{mn}(x)dx$ $(i = x, y)$, which are given by

$$[\alpha_x]_{mn} = iAev_F\frac{2}{L}\int_0^L \sin(k_m x)\cos(k_n x)dx,$$
$$[\alpha_y]_{mn} = iAev_F\frac{2}{L}\int_0^L \sin(k_m x)\sin(k_n x)dx, \quad (8)$$

where $v_F \equiv 3\gamma a_{cc}/2\hbar$. It is straightforward to show $[\alpha_x]_{mn} = iev_F A(2/\pi)\Delta n^{-1}$ by using eq. (4), and $[\alpha_y]_{mn} = iev_F A\delta_{mn}$ owing to the orthogonality condition. Similarly, the local electronic current component at a B-atom is written as

$$\mathbf{J}^B_{k_m k'_y s', k_n k_y s}(\mathbf{r}_B) = -ie\frac{\gamma}{\hbar}\Psi^B_{k_m k'_y s'}(\mathbf{r}_B)^\dagger \times$$
$$\left\{\sum_{a=1,2,3}\mathbf{r}_a\Psi^A_{k_n k_y s}(\mathbf{r}_B - \mathbf{r}_a)\right\}, \quad (9)$$

where $\mathbf{r}_B$ denotes the position of a B-atom. We define the current and amplitude for a B-atom as $\int \mathbf{J}^B_{k_m k'_y s', k_n k_y s}(\mathbf{r}_B)dy = \delta_{k'_y k_y}\frac{s'}{2}e^{-i\Theta(k_n, k_y)}\mathbf{j}^B_{mn}(x)$ and $[\beta_i]_{mn} = \int A_i(x)\mathbf{e}_i \cdot \mathbf{j}^B_{mn}(x)dx$, respectively. We obtain

$$[\beta_x]_{mn} = iAev_F\frac{2}{L}\int_0^L \sin(k_m x)\cos(k_n x)dx,$$
$$[\beta_y]_{mn} = -iAev_F\frac{2}{L}\int_0^L \sin(k_m x)\sin(k_n x)dx. \quad (10)$$

The optical transition amplitude for A-GNR is constructed from the sum of the current components, $\iint \mathbf{J}^A_{k_m k_y s', k_n k_y s}(\mathbf{r}_A)dxdy$ and $\iint \mathbf{J}^B_{k_m k_y s', k_n k_y s}(\mathbf{r}_B)dxdy$, as

$$M_i(k_m k_y s', k_n k_y s) =$$
$$\frac{1}{2}\left(se^{i\Theta(k_m, k_y)}[\alpha_i]_{mn} + s'e^{-i\Theta(k_n, k_y)}[\beta_i]_{mn}\right). \quad (11)$$

By comparing eq. (8) with eq. (10), we see that $[\beta]$ and $[\alpha]$ are related to each other via

$$[\beta_x]_{mn} = [\alpha_x]_{mn}, \quad [\beta_y]_{mn} = -[\alpha_y]_{mn}. \quad (12)$$

Then, the matrix element of eq. (11) may be written in a more compact form (in $ev_F A$ units) as

$$M_x(k_m k_y s', k_n k_y s) = \frac{i}{\pi\Delta n}\left(se^{i\Theta(k_m, k_y)} + s'e^{-i\Theta(k_n, k_y)}\right),$$
$$M_y(k_m k_y s', k_n k_y s) = \delta_{mn}\frac{i}{2}\left(se^{i\Theta(k_m, k_y)} - s'e^{-i\Theta(k_n, k_y)}\right). \quad (13)$$

Equation (13) is the optical matrix elements for A-GNRs. This result was used to explain the optical absorption spectra in ref. 12.

The matrix elements for Z-GNRs are obtained by repeating a similar calculation to that given above. A standing wave for Z-GNRs is formed by the superposition of two waves propagating in opposite y-directions. Suppose that an incident wave has a wavevector k_y in a direction perpendicular to the edge, then the wavevector of the reflected wave is given by $-k_y$ as a result of momentum conservation. The possible superpositions are

$$\psi_{k_y}(y)\frac{1}{\sqrt{2}}\begin{pmatrix}e^{-i\Theta(k_x, k_y)}\\ s\end{pmatrix} \pm \psi_{-k_y}(y)\frac{1}{\sqrt{2}}\begin{pmatrix}e^{-i\Theta(k_x, -k_y)}\\ s\end{pmatrix}. \quad (14)$$

Here, we assume that the zigzag edges appear at $y = 0$ and $y = L$, and consider a case where the zigzag edge at $y = 0$ ($y = L$) consists of A-atoms (B-atoms). Then, the electron wavefunction at the B-atoms should vanish at the edge ($y = 0$), and the antisymmetric combination is selected. Thus, the standing wave for Z-GNRs is written as

$$\Psi_{k_x k_y s}(x, y) = \psi_{k_x}(x)\frac{1}{\sqrt{L}}\begin{pmatrix}\sin[k_y y - \Theta(k_x, k_y)]\\ s\sin(k_y y)\end{pmatrix}. \quad (15)$$

The boundary condition should also be imposed at $y = L$ as $\Psi^A_{k_x k_y s}(x, L) = 0$, by which k_y is quantized according to $k_n L - \Theta(k_x, k_n) = n\pi$. Using the wavefunction $\Psi_{k_x k_n s}(x, y)$, we obtain the optical matrix element,[12]

$$M_x(k_x k_m s', k_x k_n s)$$
$$=\frac{i}{2}\left(s\cos\Theta_m + s'\cos\Theta_n\right)[\alpha_y]_{mn}$$
$$-\frac{i}{2}\left(s\sin\Theta_m[\alpha_x]_{nm} + s'\sin\Theta_n[\alpha_x]_{mn}\right),$$
$$M_y(k_x k_m s', k_x k_n s)$$
$$=\frac{1}{2}\left(s\cos\Theta_m - s'\cos\Theta_n\right)[\alpha_y]_{mn}$$
$$-\frac{1}{2}\left(s\sin\Theta_m[\alpha_x]_{nm} - s'\sin\Theta_n[\alpha_x]_{mn}\right), \quad (16)$$

where we abbreviate $\Theta(k_x, k_n)$ as Θ_n and use the fact that $k_x \approx k_F$ to obtain the right-hand side. For an interband transition ($s = -1$ and $s' = 1$), we see that the wavenumber selection rule is given by $\Delta n = \pm 1, \pm 3, \ldots$ ($\Delta n = 0$) when the polarization of an incident light is set parallel (perpendicular) to the zigzag edge, which is a 90° rotation of polarization with respect to the selection rule for A-GNRs. For an intra-band transition ($s = s'$), the selection rule for wavenumber exhibits a 90° rotation of polarization with respect to the Δn-selection rule for an inter-band transition. This additional change in the polarization dependence is a characteristic feature specific to Z-GNRs, not shown in the Δn-selection rule for A-GNRs.

In Table I, we show our results for the electron-photon matrix elements for GNRs, where we pay special attention to the change in wavenumber Δn. By replacing $\varphi_n(x)$ in eq. (5) with $\psi_n(x)$, we see that the polarization dependence of the Δn-selection rule for CNTs is irrelevant to the chirality. The existence of the edge and the resultant formation of the chirality-dependent standing wave are important to obtaining the chirality-dependent Δn-selection rule.

Finally, we briefly mention that this method is applicable to an electron-phonon interaction. A relative displacement vector for an optical phonon mode $\mathbf{u}(\mathbf{r}, t)$

Table I. Polarization dependence of Δn for the possible inter-band optical transition. "para" ("perp") means that the polarization is parallel (perpendicular) to the edge (axis) of a GNR (CNT). For GNRs, Δn induced by an electron-phonon interaction follows the same rule, where "para" ("perp") means the direction of the vibration.

	A-GNRs	Z-GNRs	CNTs
para	$\Delta n = 0$	$\Delta n = \pm 1, \pm 3, \ldots$	$\Delta n = 0$
perp	$\Delta n = \pm 1, \pm 3, \ldots$	$\Delta n = 0$	$\Delta n = \pm 1$

($\equiv \mathbf{u}_\mathrm{A} - \mathbf{u}_\mathrm{B}$) changes the hopping integral from γ to $\gamma + g\mathbf{u}(\mathbf{r}, t) \cdot (\mathbf{r}_a/a_\mathrm{cc})$, where g is a coupling constant, and induces a deformation current. The current induced at an A-atom by the lattice deformation $\mathbf{u}(\mathbf{r})$ is given as $\mathbf{J}^\mathrm{A}_{\mathbf{k}'s',\mathbf{k}s}(\mathbf{r}_\mathrm{A})$ by replacing $-e\gamma$ with g/a_cc. The current induced at a B-atom is given by $-\mathbf{J}^\mathrm{B}_{\mathbf{k}'s',\mathbf{k}s}(\mathbf{r}_\mathrm{B})$, where the extra minus sign originates from the fact that $\mathbf{u}(\mathbf{r}, t)$ changes its sign when we replace A and B-atoms: the interaction must be symmetric with respect to the change of A and B as $(\mathbf{J}^\mathrm{A} - \mathbf{J}^\mathrm{B}) \cdot (\mathbf{u}_\mathrm{A} - \mathbf{u}_\mathrm{B})$. Therefore, the transition amplitude is constructed from the difference between the current components,

$$\iint \left\{ \mathbf{J}^\mathrm{A}_{\mathbf{k}'s',\mathbf{k}s}(\mathbf{r}_\mathrm{A}) - \mathbf{J}^\mathrm{B}_{\mathbf{k}'s',\mathbf{k}s}(\mathbf{r}_\mathrm{B}) \right\} dx dy. \qquad (17)$$

Since the minus sign is taken into account as $s' \to -s'$ in Eqs. (13) and (16), we conclude that the electron-phonon matrix element for an intra-band (inter-band) transition is the same as the electron-photon matrix element for an inter-band (intra-band) transition, except for a numerical factor. Thus, the selection rule for the wavenumber of a phonon mode whose vibrational direction is either parallel or perpendicular to the edge allows a non-zero shift $\Delta n = $ odd in the wavenumber of an electron (see Table I).

In conclusion, the electronic standing waves in GNRs undergo a change in wavenumber through an optical, inter-band transition when the polarization of an incident light is perpendicular (parallel) to the armchair (zigzag) edge. The origin of the shift in wavenumber is attributed to the microscopic topology of the lattice, in that the standing wave has different probability amplitudes at adjacent sites in a chirality dependent manner. Thus, a change in wavenumber is a universal phenomenon in GNRs. The universality is also recognized for electron-phonon interactions.

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